

EXHIBIT 3

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Ink-jet printing on ceramics

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There is a potential market in digital color printing on ceramic media. One obvious application is visual arts (painting on porcelain, for example, for making tableware or custom tiles). Another application could be street or road signage, etc. Glazes for coloring ceramics contain several components, which can be loosely divided into host and chromophore. The chromophores in ceramic glazes can be one or more of the salts of transition metals, such as Fe, Cr, Mn, Ni, Co, Cu, V, Ce, Nd. These chromophores are then mixed with salts and oxides, such as Al_2O_3 , SiO_2 , SnO_2 , TiO_2 , ZrSiO_4 , MgAl_2O_4 . The glazes can have basic components and acidic components. The basic components can be carbonates, such as CaCO_3 or Na_2CO_3 . And for the acids, one can use SiO_2 , TiO_2 and SnO_2 . The typical content of a chromophore in a glaze is ca. 3 wt% (per dry weight only) and could be applied by inkjet.

There is a considerable number of the glaze recipes published, see e. g., Charles McKee, Ceramics Handbook, Star Publishing company Belmont, CA, 1984, and Greg Daly, Glazes and Glazing Techniques, 1995, Kangaroo Press, Australia. Normally, glaze components are mixed, dispersed in water and then applied to ceramics by spraying, dipping or by a brush. Then the piece is heated in the oven at 700–1300 C, depending on the glaze composition for several hours until the glaze melts.

The idea is to make the chromophore of the glaze ink-jettable and to apply it onto the ceramic that has been pre-coated with an unfired glaze. The glaze can be applied in the normal manner as a dip, brush or spray coat. For example, one can take a white glaze of the following composition (as described in McKee's book):

Nepheline Syenite 30%
Whiting 26%
Silica 30%
Kaolin 14%

The glaze would be applied, the water evaporated and then a pattern applied with an ink-jettable chromophore.

The jettable chromophore may be made up of pigment dispersions or water soluble transition metal salts. The jettable chromophore may need additives and binders, such as polyvinyl alcohol, CMC, or starches to help the pigment particles or soluble salts to stick to the unfired glazed ceramic. These binders would be removed during the firing in the furnace.

The jettable chromophore could also be printed onto a substrate such as plastic, paper or cloth. This printed substrate could then be applied directly to piece and overglazed or adhered to a piece that has already had glaze applied. Subsequent firing would "burn out" the substrate leaving the chromophore which would color the glaze.

In another embodiment, a glaze is made to be applied by a ink-jet technique which already includes the chromophore. This technique may not be advantageous since the glaze ink-flux may be too high for normal ink jet applications.

Of course, underprinting can be also used

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Next experiment

5 cm x 5 cm tile was covered with a Mayo Series 2000 Glaze S-2565 (Cloud White). The sample was dried in air I spiked the surface with $\text{Cu}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$, and $\text{Co}(\text{NO}_3)_2$. The salts were dissolved in Mount vehicle at 3%.

$\text{O} \leftarrow \text{O}$	Cu^{2+}
$\text{O} \leftarrow \text{O} \leftarrow$	Cr^{3+}
$\text{O} \leftarrow \text{O} \leftarrow \text{O} \leftarrow$	Fe^{3+}
$\text{O} \leftarrow \text{O} \leftarrow$	Co^{2+}

On the next tile, I "underprinted" the ~~spiked~~ salts with 1% Na_2CO_3 (1 drop + 1 drop),

0	0	0	Cu
0	0	0	Cr
0	0	0	Fe
0	0	0	Co

1 drop \approx 0.1 ml Na_2CO_3 was dissolved in mount vehicle

Results. After firing, the following results are seen. Cu became light blue. Chromium became

green. Fe became slightly brown. Co became blue. Adding Na_2CO_3 intensified all the colors. T $\sim 1000^\circ\text{C}$, ~ 10 hrs

Nice glaze - the only problem could be the rate flux. T Page N

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